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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08J 3/20, C08K 9/04, 9/08 — A1

(11) International Publication Number: WO 00/29467

(43) International Publication Date: 25 May 2000 (25.05.00)

(21) International Application Number: PCT/US99/25974

(22) International Filing Date: 4 November 1999 (04.11.99)

(30) Priority Data:

60/107,235	5 November 1998 (05.11.98)	US
60/108,979	18 November 1998 (18.11.98)	US

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: NANOCOMPOSITE

(57) Abstract

The instant invention in one embodiment is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoplastic polymer. The process includes the step of mixing the polyvalent anionic polymer edge coated quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer. The instant invention in another embodiment is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoset polymer. The process of this embodiment includes the steps of: (a) mixing the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer; and (b) curing the thermoset prepolymer to set the thermoset polymer. The instant invention in yet another embodiment is a composition including (a) a polymer; and (b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material. The instant invention in further yet another embodiment is a process for producing a nanocomposite polymer, including the steps of: (a) mixing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a monomer; and (b) polymerizing the monomer.

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INTERNATIONAL SEARCH REPORT

Inte rna d Application No
PCT/US 99/25974

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J3/20 C08K9/04 C08K9/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 558 075 A (SUSS NAOMI R ET AL) 10 December 1985 (1985-12-10) claims 1,2	10,12,13
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 March 2000	06/04/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Siemens, T

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/25974

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NANOCOMPOSITE

This invention relates to polymers reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymers.

Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of preferably single layers of exfoliated silicate material dispersed in a given volume of continuous polymer matrix. United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, and United States Patent Application Serial Number 034,620 filed December 31, 1996. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower weight percent of filler than conventionally filled polymers. Other United States Patents disclosing nanocomposites include 4,810,734 and 3,516,959. Edge coating of multi-layer silicate material is known, see United States Patent 4,434,075.

However, it can be difficult to get the multi-layer silicate material to exfoliate into the polymer.

The instant invention is a solution, at least in part, to the above stated problem. In one embodiment, the instant invention is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoplastic polymer. The process comprises the step of: mixing the polyvalent anionic polymer edge coated quaternary ammonium intercalated multi-layered silicate material with the termoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer.

The instant invention in another embodiment is a process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoset polymer. The process of this embodiment comprises the steps of: (a) mixing the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer; and (b) curing the thermoset prepolymer to set the thermoset polymer.

The instant invention in yet another embodiment is a composition comprising: (a) a polymer; and (b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

The instant invention in further yet another embodiment is process for

producing a nanocomposite polymer, comprising the steps of: (a) mixing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a monomer; and (b) polymerizing the monomer.

Montmorillonite clay (a multi-layered silicate material) is stirred in water with an excess of 3,400 molecular weight sodium polyacrylate (a polyvalent anionic copolymer of mole ration 1:1 of ethylene and acrylic acid) available from the Rhone-Poulenc Company to edge treat the clay. The edge treated clay is then stirred with an excess of a mixed quaternary ammonium compound (68 percent bis hydroxyethyl, dodecyl, methyl-quaternary ammonium compound and 32 percent bis hydroxy C-6 to C-9, dodecyl, methyl-quaternary ammonium compound) to produce a polyacrylate edge coated quaternary ammonium intercalated montmorillonite. The polyacrylate edge coated quaternary ammonium intercalated montmorillonite is washed with water and dried. Ninety five parts of ethylene adipate thermoplastic polyurethane (available from The Dow Chemical Company) is melted (or softened) in a polymer mixer at 160 degrees Celsius at 200 rpm. Five parts of the dried polyacrylate edge coated quaternary ammonium intercalated montmorillonite, as described above in this paragraph, is added to the mixer and mixed for five minutes. Transmission light microscopic examination of the product shows significantly fewer one hundred micrometer sized clay clusters relative to the use of non-edge coated material. Transmission electron microscopic examination of the product shows single and multiple layer exfoliation of the silicate layers of the montmorillonite. The layers are counted in a representative view. Most preferably, more of the layers are present as single layers than are present as multiple layers. In any event the dispersion of the layers into the polymer is improved using the instant invention relative to the use of a non-edge-coated material.

Polyvalent anionic organic materials are organic chemicals that have more than one carboxylic acid or other anionic substituant such as a sulfonate or a phosphonate. Preferably, the polyvalent anionic organic material is a polyvalent anionic polymer. Most preferably, the polyvalent anionic organic material is polyacrylic acid. However, the specific polyvalent anionic organic material used in the instant invention is not critical and can include, without limitation thereto, for example, copolymers of styrene and acrylic acid or styrene and sulfoethylmethacylate.

The above referred to '000 patent and the '620 patent application list exemplary multi-layered silicate materials required in the instant invention. For example, the multi-layered silicate material can be, without limitation thereto: montmorillonite; nontronite; beidellite; volkonskoite; hectorite saponite; sauconite; magadiite; medmontite; kenyaite;

laponite, mica, fluoromica and vermiculite. The above referred to '000 patent and '620 patent application also lists exemplary onium or quaternary ammonium compounds required in the instant invention. For example, the onium compound can be, without limitation thereto, quaternary ammonium compounds having octadecyl, hexadecyl, tetradecyl or dodecyl moieties. However, the specific multi-layered silicate material or onium compound used in the instant invention is not critical.

However, it should be understood that it is preferable to use polar substituted quaternary ammonium compounds with relatively polar polymers such as nylons and polyurethanes. Similarly, it is preferable to use non-polar substituted quaternary ammonium compounds with relatively non-polar polymers such as polypropylene and polyethylene. The terms "polar" and "non-polar" are used in their conventional sense. For example, a polar substituted quaternary ammonium compound is a quaternary ammonium compound having a hydroxy ethyl (C2OH) or hydroxy hexyl (C6OH) substituent(s) .

The selection of a preferred quaternary ammonium compound is aided by comparing the electron photomicrographs of the nanocomposites made using the quaternary ammonium compounds being tested in the instant invention to determine which quaternary ammonium compound(s) give the greatest degree of exfoliation of the multi-layered silicate. Of course, physical property improvement of the nanocomposite v. the base polymer is the final objective of the instant invention but such improvement is often a function of the degree of exfoliation of the multi-layered silicate.

In addition to mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a molten thermoplastic polymer, the instant invention also includes mixing the polyvalent anionic organic quaternary ammonium intercalated multi-layered silicate material with a monomer(s) or thermoset prepolymer(s) followed by the polymerization of the monomer(s)/prepolymer(s).

1. A process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoplastic polymer, the process comprising the step of: mixing the polyvalent anionic polymer edge coated quaternary ammonium intercalated multi-layered silicate material with the thermoplastic polymer at a temperature greater than the melting or softening point of the thermoplastic polymer.

2. The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate; and blends thereof.

3. The process of Claim 1 or Claim 2, wherein the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material exfoliates to produce single layers of silicate material and multiple layers of silicate material, the weight percent of the single layers of silicate material being greater than the weight percent of the multiple layers of silicate material.

4. The process of Claim 1 or Claim 3, wherein the thermoplastic polymer is a blend of thermoplastic polymers.

5. A process for producing a nanocomposite polymer by dispersing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material into a thermoset polymer, the process comprising the steps of:

(a) mixing the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a thermoset prepolymer;

(b) curing the thermoset prepolymer to set the thermoset polymer.

6. The process of Claim 5, wherein the thermoset polymer is selected from the group consisting of a thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

7. The process of Claim 5 or Claim 6, wherein the polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material exfoliates in step (a) to produce single layers of silicate material and multiple layers of silicate material, the weight percent of the single layers of silicate material being greater than the weight percent of the multiple layers of silicate material.

8. The process of Claim 5 or Claim 7, wherein the thermoset polymer is a blend of thermoset polymers.

9. The process of Claim 1, wherein the thermoplastic polymer is selected from the group consisting of polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers and thermoplastic elastomers and blends thereof.

10. A composition comprising:

(a) a polymer; and

(b) a multi-layered silicate material dispersed in the polymer, the multi-layered silicate material having edges, at least a portion of the edges of the multi-layered silicate material being bound to a polyvalent anionic organic material.

11. The composition of Claim 10, wherein at least about one half of the edges of the multi-layered silicate material are bound to the polyvalent anionic organic material.

12. The composition of Claim 10 or Claim 11, wherein the polymer is selected from the group of thermoplastic polymers and thermoset polymers and blends thereof.

13. The composition of Claim 12, wherein the thermoplastic polymers and thermoset polymers are selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers, thermoset epoxy, a thermoset phenolic, a thermoset urethane, a thermoset rubber and blends thereof.

14. The process of Claims 1-9, wherein the polyvalent anionic organic is a polyacrylate.

15. The composition of Claims 10-13, wherein the polyvalent anionic organic is a polyacrylate.

16. A process for producing a nanocomposite polymer, comprising the steps of:

(a) mixing a polyvalent anionic organic edge coated quaternary ammonium intercalated multi-layered silicate material with a monomer; and

(b) polymerizing the monomer.

17. The process of Claim 16, wherein the monomer is a blend of monomers.

18. The process of Claim 16, wherein the polymer is selected from the group consisting of a thermoplastic urethane, a thermoplastic epoxy, a thermoplastic polyester, a thermoplastic nylon, a thermoplastic polycarbonate, polypropylene, polyethylene, polystyrene, polystyrene copolymers, acrylic polymers, acetyl polymers, thermoplastic elastomers,